Synthesis of Group 4 Complexes that Contain the Diamidoamine Ligands, [(2,4,6-Me₃C₆H₂NCH₂CH₂)₂NR]²⁻ ([Mes₂N₂NR]²⁻; R = H or CH₃), and Polymerization of 1-Hexene by Activated [Mes₂N₂NR]ZrMe₂ Complexes
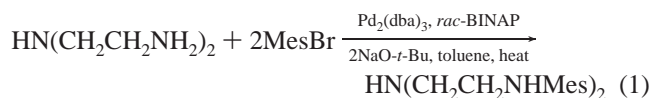
Lan-Chang Liang,[†] Richard R. Schrock,*,[†]
William M. Davis,[†] and David H. McConville[‡]

*Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Exxon Chemical Company
5200 Bayway Dr., Baytown, Texas 77522*

Received October 16, 1998

Several types of "diamido/donor" ligands have been synthesized in the last several years and attached to group 4 metal complexes, often with the intent of preparing new group 4 olefin polymerization catalysts.[1] We have been interested in zirconium complexes that contain diamido/ether ligands ([(t-BuN-o−C₆H₄)₂O]²⁻ or [(ArylNCH₂CH₂)₂O]²⁻)[1e,f,k,m] as catalysts for the polymerization of α olefins, especially since in the first case the polymerization of up to 500 equiv of 1-hexene has been found to take place in a living manner at 0 °C via 1,2-insertion of the olefin into the cationic alkyl complex.[1e,f] We became interested in diamido/donor ligands in which the central donor *cannot* readily attain a planar geometry. We report here zirconium complexes that contain the [(2,4,6-Me₃C₆H₂NCH₂CH₂)₂NR]²⁻ ([Mes₂N₂NR]²⁻; R = H or Me) ligand, along with [Mes₂N₂NH]TiMe₂ and [Mes₂N₂NH]HfMe₂ complexes, and the activation of zirconium dimethyl complexes for the polymerization of 1-hexene at temperatures up to 30 °C.

Many amines can now be arylated in a palladium-catalyzed reaction.[2] We have found that diethylenetriamine can be doubly arylated readily using mesityl bromide in a procedure that is analogous to that reported in one of several recent publications by Buchwald.[2c] The yield of H₂[Mes₂N₂NH] (eq 1) is virtually

$$HN(CH_2CH_2NH_2)_2 + 2MesBr \xrightarrow[\text{2NaO-}t\text{-Bu, toluene, heat}]{\text{Pd}_2(\text{dba})_3, \, rac\text{-BINAP}} HN(CH_2CH_2NHMes)_2 \quad (1)$$

quantitative and the reaction has been carried out without complications on a 100 g scale. Synthesis of the analogous *o*-tolyl-substituted diethylenetriamine (along with other arylated amines)

using similar methods has been reported recently,[3] as has arylation of triethylenetetramine.[4]

The [Mes₂N₂NH]²⁻ ligand was first attached to zirconium using the now familiar Zr(NMe₂)₄ route shown in eq 2. Both [Mes₂N₂-

$$Zr(NMe_2)_4 \xrightarrow[-2Me_2NH]{H_2[Mes_2N_2NH]}$$

$$[Mes_2N_2NH]Zr(NMe_2)_2 \xrightarrow[-2Me_2NTMS]{2TMSCl} [Mes_2N_2NH]ZrCl_2 \quad (2)$$

NH]Zr(NMe₂)₂ and [Mes₂N₂NH]ZrCl₂ have mirror symmetry according to NMR data, although it is likely (on the basis of a dimeric structure observed for [(t-BuN-*o*-C₆H₄)₂O]ZrCl₂[5]) that the latter is a dimer containing two bridging chlorides in the solid state. In [Mes₂N₂NH]Zr(NMe₂)₂ the two dimethylamido groups are inequivalent (resonances at 3.05 and 2.28 ppm), consistent with no rapid inversion of configuration at the central nitrogen donor.[6] The NH resonance is found as a broadened singlet at 1.80 ppm. The mesityl rings do not rotate rapidly on the NMR time scale about the N−Cᵢₚₛₒ bonds in either [Mes₂N₂NH]Zr(NMe₂)₂ or [Mes₂N₂NH]ZrCl₂.[7] These data are consistent with either a *fac* or a *mer* arrangement of the [Mes₂N₂NH]²⁻ ligand in each compound, as long as the central nitrogen donor remains bound.

The reaction between [Mes₂N₂NH]ZrCl₂ and 2 (or more) equiv of MeMgI in ether produces white crystalline [Mes₂N₂NH]ZrMe₂ in high yield. The inequivalent ZrMe resonances are found at 0.24 and 0.07 ppm in the proton NMR spectrum of [Mes₂N₂NH]-ZrMe₂ in C₆D₆, and the NH proton resonance is found at 1.16 ppm. [Mes₂N₂NH]ZrMe₂ is relatively stable in solution, although it decomposes slowly to a molecule that has yet to be identified. It is interesting to note that the central NH proton is not removed readily by MeMgI in ether at room temperature. However, it *is* removed by LiMe to give what we formulate as [(MesNCH₂CH₂)₂NLi]ZrMe₂. Addition of MeI to "[(MesNCH₂CH₂)₂NLi]ZrMe₂" then gives [Mes₂N₂NMe]ZrMe₂ in high yield.

An X-ray study of [Mes₂N₂NMe]ZrMe₂ reveals a structure (Figure 1) in which the three nitrogens lie in a plane that bisects the C(1)−Zr−C(2) angle, i.e., a *mer* structure. The donor amine nitrogen nevertheless is virtually tetrahedral (C−N−C = 109°, 109°, and 112°). The Zr−Nₐₘᵢₙₑ bond length, Zr−Nₐₘᵢdₒ bond lengths, Zr−Me bond lengths, and C−Zr−C, N−Zr−N, and Zr−N−C angles are all typical of diamido/N_donor complexes having a *mer* geometry.[1h,8] The *mer* structure of [Mes₂N₂NMe]ZrMe₂ contrasts with the *fac* structures found for [(Me₃SiNCH₂CH₂)₂-NSiMe₃]ZrX₂ (X = halide or alkyl) complexes.[1b,d]

The apparent stability and ease of formation of [Mes₂N₂NH]-ZrMe₂ led us to attempt to form it "directly" from ZrCl₄, H₂[Mes₂N₂NH], and MeMgI. Addition of ZrCl₄ to H₂[Mes₂N₂-NH] in ether resulted in the formation of a precipitate in which we assume the ligand has been at least partially attached to the metal. Subsequent addition of 4 equiv of MeMgI followed by a standard workup yielded [Mes₂N₂NH]ZrMe₂ in ∼40% yield on a scale of ∼0.6 g of product. A similar "direct" approach also gave red [Mes₂N₂NH]TiMe₂ in ∼35% yield and white [Mes₂N₂-
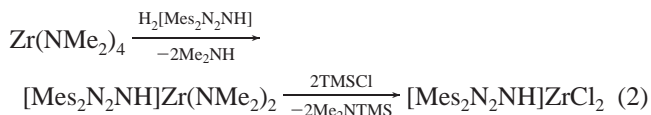
† Massachusetts Institute of Technology.
‡ Exxon Chemical Company.
(1) (a) Clark, H. C. S.; Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B.; Wainwright, A. P. *J. Organomet. Chem.* **1995**, *501*, 333. (b) Cloke, F. G. N.; Hitchcock, P. B.; Love, J. B. *J. Chem. Soc., Dalton Trans.* **1995**, 25. (c) Horton, A. D.; de With, J. *Chem. Commun.* **1996**, 1375. (d) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (e) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830. (f) Baumann, R.; Schrock, R. R. *J. Organomet. Chem.* **1998**, *557*, 69. (g) Guérin, F.; McConville, D. H.; Payne, N. C. *Organometallics* **1996**, *15*, 5085. (h) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1996**, *15*, 5586. (i) Schattenmann, F. J.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 989. (j) Friedrich, S.; Schubart, M.; Gade, L. H.; Scowen, I. J.; Edwards, A. J.; McPartlin, M. *Chem. Ber. Rec.* **1997**, *130*, 1751. (k) Aizenberg, M.; Turculet, L.; Davis, W. M.; Schattenmann, F. S.; Schrock, R. R. *Organometallics* **1998**, *17*, 4795. (l) Male, N. A. H.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2487. (m) Schrock, R. R.; Schattenmann, F.; Aizenberg, M.; Davis, W. M. *Chem. Commun.* **1998**, 199.
(2) (a) Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2046. (b) Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (c) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215.

(3) Hong, Y.; Senanayake, C. H.; Xiang, T.; Vandenbossche, C. P.; Tanoury, G. J.; Bakale, R. P.; Wald, S. A. *Tetrahedron Lett.* **1998**, *39*, 3121.
(4) Greco, G. E.; Popa, A. I.; Schrock, R. R. *Organometallics* **1998**, *17*, 5591.
(5) Baumann, R. Ph.D. Thesis, Massachusetts Institute of Technology, 1998.
(6) Inversion has been observed in titanium complexes that contain the [(Me₃SiNCH₂CH₂)₂NSiMe₃]²⁻ ligand as a consequence of the relatively poor basicity of the central nitrogen donor containing the bulkyl TMS substituent and relatively weak Ti−N donor bond.[1a]
(7) (a) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 5478. (b) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241. (c) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008.
(8) Schrock, R. R.; Lee, J.; Liang, L.-C.; Davis, W. M. *Inorg. Chim. Acta* **1998**, *270*, 353.
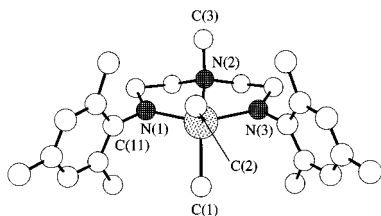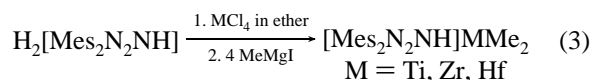
Figure 1. A Chem 3D drawing of the structure of [Mes$_2$N$_2$NMe]ZrMe$_2$ (N(1)−Zr−N(2) = 70.26(11)°; Zr−N(1)−C(11) = 118.8(3)°; M−N(2) = 2.373(5) Å; M−N$_{ax}$ = 2.095(4) Å; N(1)−M−N(3) = 140.5(2)°; M−C = 2.240(7), 2.265(7) Å; C(1)−M−C(2) = 103.2(3)°).

Table 1. Characterization of the Poly(1-hexene) Prepared with [Mes$_2$N$_2$NR]ZrMe$_2$ (R = H (**A**), Me (**B**)) Initiators[a]

no.	precursor	equiv	T (°C)/ min	MW(calcd)[b]	$10^{-2}M_n$	$10^{-2}M_w$	PDI
1	**A**	134	0/60	11300	125[c]	162	1.3
2		313	0/60	26300	170[d]	209	1.2
3		626	0/60	52700	127[d]	172	1.4
4	**B**	139	0/60	11700	167[c]	192	1.1
5		278	20/60[e]	23400	321	400	1.2
6		325	0/60	27400	287[d]	396	1.4
7		325	20/60[e]	27400	258[d]	398	1.5
8		649	0/60	54600	291[c]	450	1.5
9		19	20/30[e]				
		259	20/60[e]	23400	265	435	1.6
10		46	20/30[e]				
		232	20/60[e]	23400	207[d]	382	1.8
11		93	20/30[e]				
		185	20/60[e]	23400	153	321	2.1
12[f]		139	20/60,[e] 65/10				
		139	20/60[e]	23400	174	213	1.4

[a] The initiator was prepared as described in the text and in the Supporting Information; yields were quantitative except in run 12. M_w and M_n were determined by a combination of light scattering and refractometry. [b] Calculated on the basis of the number of monomers added. [c] Average of three determinations for a single sample. [d] Average of two determinations for a single sample. [e] Reactions were initiated at ~20 °C, but the temperature increased rapidly to as much as 30 °C within ~1 min. [f] The yield was ~65% and the molecular weight distribution was bimodal; the values for M_n, M_w, and PDI refer to the higher molecular weight peak.

NH]HfMe$_2$ in ~35% yield on similar small scales (eq 3). The

$$\text{H}_2[\text{Mes}_2\text{N}_2\text{NH}] \xrightarrow[\text{2. 4 MeMgI}]{\text{1. MCl}_4 \text{ in ether}} [\text{Mes}_2\text{N}_2\text{NH}]\text{MMe}_2 \quad (3)$$
$$\text{M = Ti, Zr, Hf}$$

preferred "direct" synthesis of [Mes$_2$N$_2$NH]ZrMe$_2$ consists of preparing the insoluble adduct in toluene (80 °C, 24 h, quantitative yield), then treating the mixture with 4 equiv of MeMgBr in ether (3.0 M). The magnesium salts were filtered off and [Mes$_2$N$_2$NH]-ZrMe$_2$ was isolated from the filtrate in 86% yield.

Addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to [Mes$_2$N$_2$NH]ZrMe$_2$ or [Mes$_2$N$_2$-NMe]ZrMe$_2$ in chlorobenzene at 0 °C yielded a yellow solution. 1-Hexene was added and the solution was kept at 0 °C for a period of 1 h.[9] The still yellow reaction mixture was then quenched with ethereal HCl and the poly(1-hexene) isolated and analyzed as described elsewhere.[1k,m] The results of analysis of the poly(1-hexene) by gel permeation chromatography are shown in Table 1 (runs 1, 2, 3, 4, 6, 8). The number average molecular weight of the poly(1-hexene) obtained was consistent with some chain termination, presumably via β elimination. However, since the yields were all quantitative, the presumed hydride product of β elimination is stable enough to begin another chain. The maximum molecular weight found employing [Mes$_2$N$_2$NMe]ZrMe$_2$ (runs 4,

(9) The choice of 1-hexene (versus propylene) is based solely on the ease of analyzing poly(1-hexene) by GPC and the relative convenience of the polymerization procedure.

6, 8) is approximately double that found employing [Mes$_2$N$_2$-NH]ZrMe$_2$, consistent with less β elimination. When a 325 equiv polymerization employing [Mes$_2$N$_2$NMe]ZrMe$_2$ is begun at ~20 °C (run 7) the results are essentially the same as those obtained at 0 °C (run 6), even though the exotherm produces a rise in temperature to ~30 °C in ~1 min under these conditions. Runs 9, 10, and 11 reveal that addition of the 1-hexene in two portions with a 30 min pause between the two additions leads to polymer with a higher PDI and a M_n corresponding approximately to the number of equivalents of monomer added in the second step. Therefore, it appears that a significant amount of β elimination takes place within ~30 min at 20−30 °C for oligomers that contain between 20 and 100 monomer units in the absence of excess monomer, but the product of β elimination is relatively stable and can generate a second chain. However, heating a sample to 65 °C for 10 min between the two additions of 1-hexene (run 12) leads to a less than quantitative yield (65%) of poly(1-hexene), consistent with a significant amount of *irreversible* decomposition of the polymerization intermediate formed from 139 equiv of monomer at 65 °C.

So far no titanium diamido/donor complexes that we have prepared in our laboratory have been found to be well-behaved initiators for the polymerization of 1-hexene.

The results described here should be compared with those found for Zr systems employing [(t-BuN-o-C$_6$H$_4$)$_2$O]ZrMe$_2$ as an initiator, which yield poly(1-hexene) via *primarily* (>95%) a 1,2-insertion process[1f] with little β elimination during synthesis of up to a 500 mer.[1e] We now believe that the [(t-BuN-o-C$_6$H$_4$)$_2$O]$^{2-}$ system is successful in part as a consequence of the significant steric hindrance afforded by *tert*-butyl substituents and the formation of relatively crowded pseudo-tetrahedral monoalkyl cations. It should be noted that a 2,1-insertion product would have a different reactivity (presumably lower) and a different stability (presumably also lower) than a 1,2-insertion product, as has been proposed in propylene polymerization systems.[10] Therefore we hypothesize that {[Mes$_2$N$_2$NR]Zr(polymer)}$^+$ intermediates become more stable toward β elimination when R is a methyl group, in part because of a lower percentage of sterically more difficult 2,1-insertions. We also propose that the pseudo-tetrahedral configuration of the bound central nitrogen donor sharply increases the tendency to form a pseudo-tetrahedral monoalkyl cationic complex in which steric crowding is exacerbated by a contraction of metal−ligand bond lengths, one in which the strength of anion binding and 2,1 "misinsertions" therefore are limited, although apparently not to the degree yet that is found in the [(t-BuN-o-C$_6$H$_4$)$_2$O]$^{2-}$ system. However, the steric bulk of the amido and amine substituents should be adjustable to the point where steric hindrance is maximized. Experiments aimed in this direction are under way.

Supporting Information Available: Experimental procedures, fully labeled ORTEP drawing, crystal data and structure refinement, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [Mes$_2$N$_2$NMe]ZrMe$_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA983636N

(10) (a) Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538. (b) Busico, V.; Cipullo, R.; Talarico, G. *Macromolecules* **1998**, *31*, 2387. (c) Busico, V.; Cipullo, R.; Talarico, G.; Segre, A. L.; Caporaso, L. *Macromolecules* **1998**, *31*, 8720. (d) Resconi, L.; Piemontesi, F.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046. (e) Guerra, G.; Longo, P.; Cavallo, L.; Corradini, P.; Resconi, L. *J. Am. Chem. Soc.* **1997**, *119*, 4394.